

# The Use of the Field Emission Electron Microscope in Adsorption Studies of W on W and Ba on W

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The chief conclusions from these studies are given in the Introduction. Table II summarizes the adsorption properties of *W* on *W* and *Ba* on *W*. These properties vary with the crystal plane and are given for five planes. The extent to which these planes develop depends on *T* and the applied field, *F*. The temperature at which *W* atoms migrate on *W* at detectable rates depends on the plane and on *F*, and varies from 800 to 1200°K.

The adsorption properties of *Ba* on *W* are quite different for the first layer than they are for subsequent layers. In the first layer for which  $\theta \leq 1$ , *Ba* forms two phases: a condensed phase in which the *Ba* forms clusters or islands having a median diameter of  $100 \times 10^{-8}$  cm, and a dispersed phase consisting of individual atoms. The temperature at which *Ba* migrates at detectable rates varies from 370 to 800°K from the 110 to the 100 plane. The evaporation rate depends on  $\theta$ . At  $\theta$  near 1.0 it is detectable at 1050°K. At 1600°K practically all the *Ba* is evaporated.

For more than one layer of *Ba* on *W*, the *Ba* forms crystallites which grow outward from the *W* surface even at room *T*. Their median diameter is about  $400 \times 10^{-8}$  cm and they disappear between 600 and 800°K.

## INTRODUCTION AND CONCLUSIONS

**E**W. MÜLLER,<sup>1</sup> in 1936, described a tube in which the field emission electrons from a very sharp tungsten point were made to impinge on a fluorescent screen and there portray a magnified image of the variation in emission density from different regions on the point. He showed that magnifications approaching a million fold could be obtained. In subsequent papers<sup>2</sup> he showed how such a tube can yield direct and striking information on the surface structure and on the effects of adsorbed films. Jenkins,<sup>3</sup> in 1943, summarized the progress to that date and showed that fields of the order of  $10^7$  volts/cm produced pronounced changes in the surface configuration. More recently F. Ashworth<sup>4</sup> has reviewed the field emission from clean metallic surfaces.

In Fig. 2, (a) and (b) are two examples of photographs of the screen when field emission electrons are drawn from a single crystal of tungsten. The bright and dark regions are caused by variations in the intensity of electron emission from different regions of the tungsten surface. From such photographs it is possible to deduce how the electron work function varies for different crystallographic planes, how adsorbed atoms change this work function, and how the surface deviates from a smooth hemisphere when the tungsten is subjected to a range of temperatures and fields.

It is quite apparent that this new and powerful tool will reveal, on an

almost atomic scale, the nature of adsorption phenomena which are basic to thermionic, photoelectric and secondary electron emission, to catalysis and also to biological processes. Unfortunately, in most of the early work the residual gas pressure in the tube was such that the surface was contaminated in a few minutes and hence the results were probably affected by this contamination. In the present investigation the vacuum conditions were improved to such an extent that the residual gas produced only barely detectable effects after about one week. Under such conditions the following observations and conclusions have been made:

(1) When a sharp point of a single crystal of tungsten is held at  $2400^{\circ}\text{K}$  until a steady state is reached, most of the surface is approximately hemispherical or more precisely paraboloidal. About 20% of the surface consists of three atomic planes which in decreasing order of size are 110, 211, and 100 planes. This is also the order of increasing intensity of field emission. The greatest intensity of emission is from the 611 direction and other directions surrounding the 100 direction. The next greatest intensity comes from the 111 direction and neighboring regions.

(2) For temperatures  $> 2400^{\circ}\text{K}$  the area of the 110, 211, and 100 planes decreases; between 2400 and  $1050^{\circ}\text{K}$  the 211 and 100 planes increase steadily in size; below  $1050^{\circ}\text{K}$  the rate of change of area is so slow that no changes are observed in one hour. These changes are ascribed to migration of  $W$  atoms on  $W$ .

(3) From 1050 to  $1200^{\circ}\text{K}$ ,  $W$  atoms migrate most easily in the 111 direction on the 211 plane. In this direction the atoms in the outermost layer contact their nearest neighbors but the rows of atoms are separated by 1.635 atom diameters. The migrated  $W$  atoms are deposited on the hemispherical surface adjoining the 211 plane and form a crescent shaped mound resulting in an abnormally high field and enhanced emission. In the region between the 211 and 110 planes,  $W$  atoms are also mobile in the 111 direction and form a series of step-like planes. In other regions the  $W$  atoms show no large scale migration. Above  $1200^{\circ}\text{K}$ ,  $W$  atoms are mobile everywhere.

(4) When fields of the order of 40 million volts/cm are applied to the surface the rate of change of the surface configuration is greatly increased and migration of  $W$  atoms can be observed in one hour on the 211 planes and near-by regions at  $800^{\circ}\text{K}$ . These changes are the same for electron accelerating and electron retarding fields. The rate of change increases rapidly with the strength of the field, perhaps as the square or cube of the field. At  $T = 1400^{\circ}\text{K}$  and for fields of  $40 \times 10^6$  volts/cm applied for hours, over half of the surface consists of planes: the 211 planes almost meet the 110 planes, and 111 and 310 planes develop. Subsequent glowing without an applied field undoes the effects produced by the field.

(5) When Ba is deposited on clean *W*, the average work function  $\varphi$  decreases from about 4.4 volts to about 2.1 volts when an optimum amount is reached at somewhere near a monomolecular layer. Further deposition increases  $\varphi$  to that of bulk Ba for which  $\varphi$  is 2.5 volts. For convenience we define the average coverage,  $\theta$ , as the Ba concentration divided by the concentration when  $\varphi$  is a minimum.

(6) For  $\theta$  from 0 to 1.0, the emission comes largely from aggregates or clusters of Ba, approximately circular in shape with diameters ranging from 40 to 200 Å and a median diameter of about 100 Å. Between 600 and 900°K these clusters are in violent agitation with the centers of a cluster appearing to shift about half a diameter. Sometimes one cluster may disappear and another one near by appear. We propose that this means that the Ba forms two phases on the tungsten surface: a condensed phase of clusters and a gaseous phase of individual Ba atoms. We propose that the centers of these clusters are irregularities on the tungsten surface where small atomic planes or facets meet to form a valley. Even a clean tungsten surface shows evidence of such irregularities whose distribution in numbers and sizes is about the same as for Ba on *W* but in which the variation in emission density is much less pronounced.

(7) For  $\theta > 1.0$ , the emission comes mostly from larger aggregates which range in size from 200 to 600 Å or more. They produce spots which are intensely bright and are in continuous agitation of flicker even at room temperature. We associate these larger bright spots with crystallites because we believe them to be caused by Ba crystals which grow out normal to the tungsten surface and thus produce extra large local fields and hence enhanced local emission. These crystallites disappear, presumably due to migration or evaporation, at temperatures from 400 to 600°K.

(8) For  $\theta < 1.0$  and *T* between 600 and 1000°K, the chief effects are due to migration of Ba from one region to another. From 600 to 700°K this migration is restricted to the 211 planes and adjoining regions in the 111 zones; the regions near 100 do not yet show migration. In any region migration starts when the Ba clusters show noticeable agitation. At 800°K cluster agitation and migration occur in all regions and Ba atoms migrate from one side of the point to the other side for a distance of 3000 Å in about 5 minutes. At 900°K the migration rate is more rapid.

(9) For  $\theta < 1.0$  and *T* between 1050 and 1600°K the chief effect is that of evaporation. This is deduced from the fact that, as the temperature is increased progressively in about 100° steps and maintained at each *T* for about 5 min., the voltage or field required to obtain an emission of say 10 microamps becomes progressively higher, presumably because  $\theta$  decreases and  $\varphi$  increases. At any one temperature, the rate of evaporation is at first quite rapid but decreases as  $\theta$  decreases. After five minutes the rate is much

less than it was in the first minute, and after about 20 minutes the rate of evaporation is so small that  $\theta$  has nearly reached a steady state. To reduce  $\theta$  still more it is necessary to increase  $T$ . At  $1600^\circ\text{K}$  nearly all the Ba has evaporated and the emission pattern looks like that of clean  $W$ . Subsequent glowing at still higher temperatures produces only small increases in  $\varphi$  and small changes in the emission pattern.

(10) For  $\theta = \text{about } .18$  and  $T = 800^\circ\text{K}$  we have observed a marked redistribution of Ba when a high field is applied: some Ba leaves the 211 and 111 regions and accumulates near the 100 regions. If the surface is then held at  $800^\circ\text{K}$  with zero field, some Ba leaves the 100 region and returns to

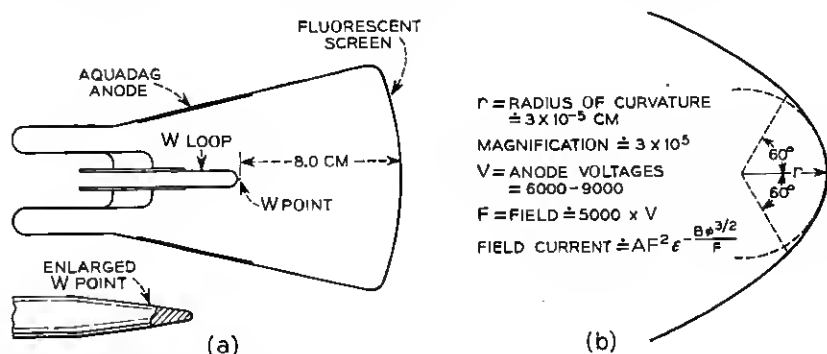


Fig. 1—(a). Cross-section of tube.

(b). Enlarged cross-section of tip of  $W$  point and values of constants.

the 211 and 111 regions. This indicates that the adsorption forces can be modified appreciably by high applied fields.

## PART I

### DESCRIPTION OF FIELD EMISSION MICROSCOPE TUBE

Figure 1(a) is a cross-section of the tube. The loop which was used to heat the point consisted of  $W$  wire 5.7 cm long and .0165 cm diameter. The  $W$  point projected about 1 mm beyond the loop. It was formed by repeatedly heating the  $W$  wire in a gas flame to oxidize it and removing the oxide with sodium nitrite. Two tantalum wire loops of  $2.0 \times 10^{-2}$  cm diameter wire are not shown. They were used to evaporate a tantalum film over most of the glass surface in order to adsorb residual gases and thus decrease the pressure. This proved to be very effective and estimated pressures of  $10^{-12}$  to  $10^{-14}$  mm Hg. were obtained. The tube also contained a source of Ba which could be deposited on part of the  $W$  point and loop. It consisted of a coil of .020 tantalum wire heavily coated with  $\text{BaO} + \text{BeO}$ . The coil con-

sisted of 8 turns, .3 cm diameter. The center of the coil was 2 cm from the point, and the axis of the coil formed an angle of about  $30^\circ$  with the axis of the tube. Since the composition of the source is essentially that of Batalum getters which are known to evaporate Ba, it is assumed that nearly pure Ba evaporated from it. There is, however, the possibility that some BaO evaporated with the Ba. The tube has been in an operable condition for about 12 years.

The tube was baked at  $400^\circ\text{C}$  for one hour. Then all the parts were glowed or heated to outgas them. It was rebaked at  $410^\circ\text{C}$  for three hrs. The *W* loop, Ta filaments, and Ba coil were heated so hot that further heating did not increase the pressure. The tube was sealed off at a pressure of  $2 \times 10^{-7}$  mm with both Ta filaments at a high temperature. Soon after the tube was sealed off the patterns for clean *W* and Ba on *W* were quite unsteady: there were rapid variations in intensity of small bright spots or flickering and there were more gradual changes in the pattern over large areas. After glowing the *W* loop, Ta filaments, and Ba coil many times and at successively higher temperatures, the flickering disappeared completely and the slow large-area changes became less pronounced or required a longer time to appear. Characteristic patterns could be reproduced at will for any particular treatment. In the early stages the clean *W* pattern changed noticeably in one minute; later, the time required for a definite change to occur increased to ten minutes, then one hour, then one day, and finally one week or even one month. The effect of the residual gas was to enlarge the 211 planes and darken the 111 zone. The effect of this residual gas could be removed at  $T = 800^\circ\text{K}$  in a minute. We suspect that the residual gas is mostly CO.

During the course of many experiments, the *W* loop was raised from 2200 to  $2800^\circ\text{K}$ . Gradually the voltage required to obtain a field emission of 10 microamps from clean *W* increased from 6000 to 9000 volts. In accordance with Mueller's results<sup>2</sup> we ascribe this to an increase in the radius of curvature of the point from 2 to  $3 \times 10^{-5}$  cm.

The lower portion of Fig. 1a shows an enlarged view of the *W* point and indicates that the tip of the point consists of a single crystal. Hence all possible crystal orientations should be represented on the surface. Figure 1b shows a still further enlargement of the tip of the point. We assume that near the tip of the point the surface is a paraboloid. If the origin is taken at the vertex, and *y* is measured along the axis and *x* perpendicular thereto, the equation for the paraboloid is

$$y = x^2/2r \quad (1)$$

where *r* is the radius of curvature of the "point." The field near such a sur-

face can be calculated if the anode is a larger paraboloid whose equation is given by

$$y = x^2/2(2d + r) \quad (2)$$

provided the origin is at its vertex,  $d$  is the distance between the two vertices, and the axes of the two paraboloids are the same. The field  $F_h$  for points at which  $y = h$ , is given by\*

$$F_h = K_h V = \frac{2V}{r(1 + 2h/r)^{1/2} \ln(1 + 2d/r)} \quad (3)$$

where  $h$  is distance along the axis of the small paraboloid. At the tip or vertex of the  $W$  point,  $h = 0$  and

$$F_0 = \frac{2V}{r \ln(1 + 2d/r)} \equiv K_0 V \quad (4)$$

$$\text{Hence } F_h = F_0 / \left(1 + \frac{2h}{r}\right)^{1/2} \quad (5)$$

For an angle of  $60^\circ$  with the axis,  $h/r = .47$  and

$$F_h = .72 F_0$$

For clean  $W$ , this predicts that the emission density at an angle of  $60^\circ$  with the axis should be .008 of the emission density along the axis. For angles less than  $10^\circ$  the field and emission densities should differ only slightly from that for the axis values. Experiment shows that these predictions are qualitatively fulfilled.

Subsequent photographs will show that for clean  $W$  most of the emission comes from regions which surround the 100 plane. For the 611 plane  $\phi = 4.4$  volts.<sup>5</sup> The area of these highly emitting regions corresponds to about  $\frac{1}{3}$  of the area of the screen which in turn corresponds to about  $\pi r^2 \text{ cm}^2$  on the  $W$  point. Hence we have taken the highly emitting area to be  $r^2 \text{ cm}^2$ . The highest emitting areas make an angle of about  $25^\circ$  with the axis of the  $W$  point or with the 110 direction. From Eq. (3) we calculate that the field is about .924 that at the tip of the point.

In order to obtain a value of  $r$ , the radius of curvature of our  $W$  point, we proceeded as follows: We observed the emission current  $i$  as a function of the applied voltage  $V$  and plotted  $\log i - 2 \log V$  vs  $1/V$ . Straight lines were obtained whose slopes and intercepts for clean  $W$  depended on the highest temperature and time at which the  $W$  loop was glowed. We then plotted a similar family of theoretical lines for various assumed values of  $r$ . The ex-

\* We are indebted to our colleague S. P. Morgan for Eqs. (1) to (4).

perimental curves agreed fairly well with the theoretical ones for both slope and intercept. The values of  $r$ , deduced from the location of the experimental lines, ranged from  $2 \times 10^{-6}$  cm for low temperature treatment to  $3 \times 10^{-6}$  cm after repeated glowing at  $2800^\circ\text{K}$ .

The theoretical family of curves was based on the Fowler-Nordheim equation modified for the electron image effect:<sup>3</sup>

$$j(\text{amps/cm}^2) = \frac{1.5 \times 10^{-6} K^2 V^2}{\varphi} \epsilon^{-(\varphi^{3/2}/KV)6.8 \times 10^7 f(x)} \quad (6)$$

in which the field  $= K \times V$  volts/cm and  $x = \frac{3.78 \times 10^{-4} \sqrt{KV}}{\varphi}$ . Nordheim<sup>6</sup> gives a table of  $f(x)$  vs  $x$ . From this we plotted  $f(x)$  vs  $KV$  for  $\varphi = 4.4$  volts, and found that for values of the field  $KV$  from 15 million to 95 million volts/cm,  $f(x)$  was given by

$$f(x) = .968 - 5.54 \times 10^{-9} KV \quad (7)$$

This range of field covers nearly all values which are usually encountered in field emission. By substituting Eq. (7) in Eq. (6) and putting  $\varphi = 4.4$  we obtain

$$j = 3.42 \times 10^{-7} K^2 V^2 \epsilon^{3.47} \epsilon^{-(6.06 \times 10^8 / KV)} \quad (8)$$

For a  $W$  point in which the major part of the current comes from an area of about  $r^2 \text{ cm}^2$  having a work function  $\varphi$  of 4.4 volts, and making an angle of about  $25^\circ$  with the axis, the current  $i$  in amperes is given by

$$\log i = -5.00 + .04 + 2 \log r + 2 \log K + 2 \log V - \frac{2.64 \times 10^8}{KV} \quad (9)$$

in which  $K$  is a function of  $r$ ,  $h$ , and  $d$  given by Eq. (3). For the experimental tube the point to anode distance was 4.0 cm. Since the field at the point will vary only slightly with the exact shape of the anode we have put  $d = 4.0$  cm. For  $r = 3 \times 10^{-6}$  cm

$$K_0 = 5300 \text{ cm}^{-1}, K_h = .924 K_0 = 4900 \text{ cm}^{-1}$$

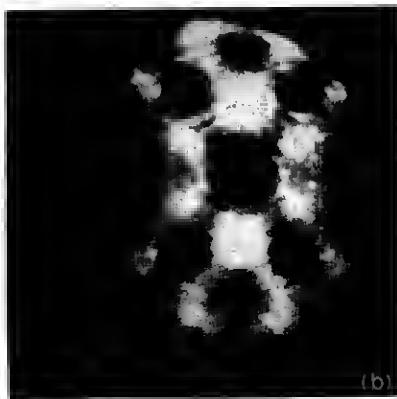
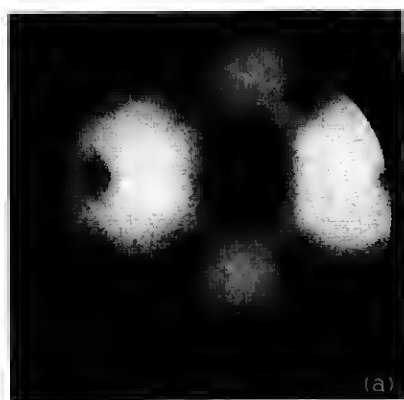
and

$$\log i = -7 + .41 + 2 \log V - 5.40 \times 10^4 / V \quad (10)$$

Similar equations can be deduced for other values of  $r$ .

From Eq. (6) it follows that the current density and hence the screen brightness depend on the work function  $\varphi$ , and the field  $KV$ : the current density increases as  $\varphi$  decreases, and increases as  $K$  increases. Since the single crystal point exposes all possible planes and since it is known that different

planes of  $W$  have different work functions, it is to be expected that different regions of the point will emit various current densities. Quantitative calculations show that the ratio of highest to lowest current densities should be at least 300. The current density might also be expected to vary if  $KV$  varies due to small local elevations or depressions from the paraboloid. Such hills and valleys or ridges might result in 10-fold variations in current density. Both types of variations are illustrated in photographs which are to follow.



NORMAL CLEAN W  
 $T = 2400^\circ \text{K}$   $V = 0$  30 SECONOS  
 $T = 300^\circ \text{K}$   $I = 40 \mu\text{A}$   $V = 9000$   
 $\frac{1}{5}$  SECONO

Ba ON ENLARGED PLANES  
 $T = 1210^\circ \text{K}$   $V = 0$  1 MINUTE  
 $T = 300^\circ \text{K}$   $I = 40 \mu\text{A}$   $V = 7500$   
 $\frac{1}{5}$  SECONO

Fig. 2—Field emission patterns from normal clean tungsten and from  $Ba$  on  $W$  with enlarged planes. Note elliptical structure around central dark region in (b). The treatment which conditioned the  $W$  point is given above the black line; the constants used in taking the photograph are given below the lines.

The various physical constants pertaining to the experimental tube are summarized in the left part of Fig. 1b. The error in the value of  $r$  is probably less than 20% and the error in the magnification is probably less than 30%.

#### FIELD EMISSION FROM A PARABOLOIDAL SURFACE OF A $W$ SINGLE CRYSTAL

Reproductions of photographs of the screen are shown in Figs. 2, (a) and (b), and 3 (a). Figure 3 (b) shows the indices of the principal regions and zones appearing in these and subsequent reproductions. For the experimental tube and for a point with a radius of curvature of  $3 \times 10^{-5}$  cm, the distance between two nearest 211 planes is about 2000 Å. Other dimensions can be scaled off on the reproductions. In these and other reproductions, the treatment given the surface is described in the upper part of the print-



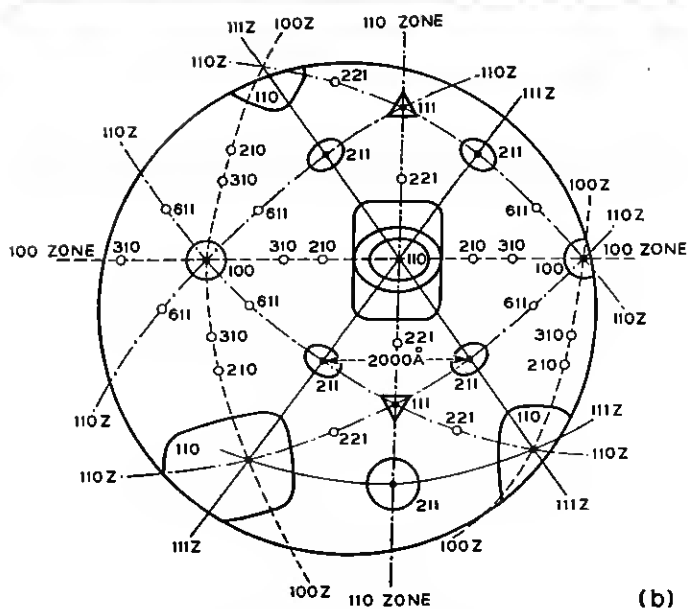
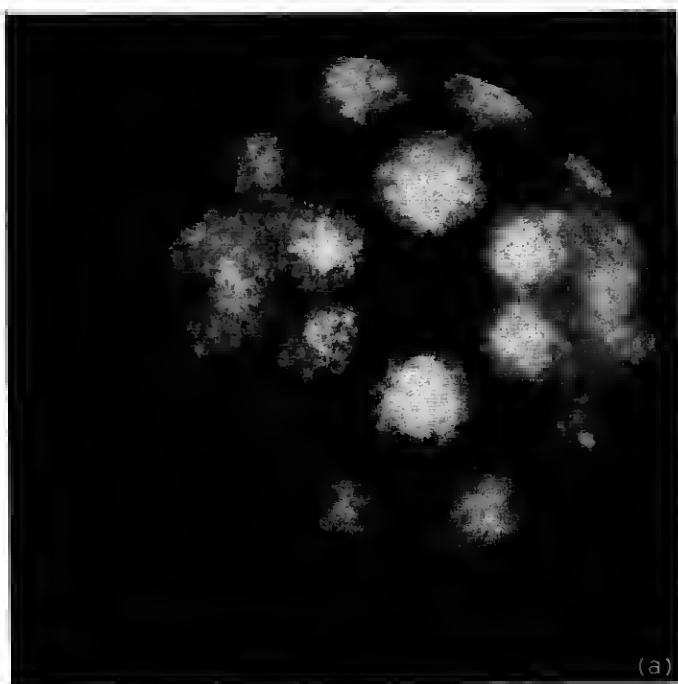


Fig. 3—(a). Pattern of *Ba* on normal clean *W*. Note granular structure due to *Ba* clusters.  
 (b). Location of principal planes and zones as they appear on the screen.

ing; the lower part describes the conditions under which the photograph was taken. For example, for Fig. 2 (a) the  $W$  point was heated to  $2400^{\circ}\text{K}$  with zero applied voltage for 30 sec. The photograph was taken with the point at room temperature, assumed to be  $300^{\circ}\text{K}$ , with  $+9000$  volts applied to the anode, while a field emission current of 40 microamps was drawn from the point, and for an exposure of  $\frac{1}{8}$  sec.

From Fig. 2(a) it is easily seen that for "normal clean  $W$ " which we define as  $W$  glowed at  $2400^{\circ}\text{K}$ , the 110, 211, and 100 regions emit poorly; the 111 region emits moderately; the greatest emission density comes from a rather broad band surrounding the 100 region. The center of this band makes an angle of about  $20^{\circ}$  with the 100 direction. The 611 plane lies in the central part of this band. In Jenkins' *Report*<sup>3</sup> it is shown that the 110, 211, and 100 dark regions are planes and that the extent of these planes can be increased by applying high positive fields while the point is at temperatures near  $1200^{\circ}\text{K}$ .

Figure 2(h) shows a photograph for a point which has been treated in this manner; Ba was then evaporated onto the  $W$  and the  $W$  loop was heated until the Ba migrated over the surface. Figure 3(a) shows the emission from migrated Ba on normal clean  $W$ . In Figs. 2(h) and 3(a) the amount of Ba is rather small, about .10 monolayer. For Ba on tungsten the emission comes from small "circular" regions with an average diameter of  $100 \text{ \AA}$ . We interpret these to be small regions in which the Ba atoms cluster together, thus reducing the work function more than in neighboring regions, and hence we call such regions clusters.

A careful inspection of the negatives for clean  $W$  show that, in regions other than the 110, 211, and 100 planes, the emission shows a granular structure with small regions of the order of  $100 \text{ \AA}$  diameter surrounded by slightly darker regions. We believe this to be due to submicroscopic facets on the paraboloidal surfaces; these facets form small hills or plateaus and valleys. On the small hills the local field is slightly greater than in the valleys and hence the emission from clean  $W$  is slightly greater than from the valleys. On the other hand we believe that the Ba atoms are held more firmly in the valleys or troughs where they can contact more  $W$  atoms, thus accounting for the Ba clusters discussed in the preceding paragraph.

Figure 2(h) also shows a series of large elliptical rings with their center in the 110 plane and their major axis in the 100 zone. The evidence for these is especially pronounced in the 111 zones. The separation between them is about  $170 \text{ \AA}$ . This suggests that the 110 plane and the region surrounding it consists of a series of plateaus of 110 planes elliptical in shape.

EFFECT OF TEMPERATURE IN DETERMINING THE SIZE OF 110,  
211 & 100 PLANES

Figure 4 shows the effect of glowing the point at temperatures from 2600 to 1200°K. In each case the temperature was held at a constant value until an approximate steady state was reached. When the photographs were taken, the applied voltages were adjusted slightly so as to maintain a constant average screen intensity. After the 1200°K glowing, the 2400°K was repeated. All the films came from the same pack and were developed together. Other tests showed that the result for a given temperature did not depend upon temperature treatments that preceded it.

From this series of tests we conclude: (1) A single crystal of tungsten which is approximately a paraboloid with a radius of curvature of  $3 \times 10^{-5}$  cm and which has been heated for approximately an hour at 2400°K, assumes a surface configuration in which 110, 211, and 100 planes develop. The remainder of the surface consists of small facets or crystal planes of the order of 100 Å across. (2) The 110 planes are rectangular in shape with rounded corners; the 211 planes are slightly elliptical; the 100 planes are circular. (3) As the temperature of glowing decreases from 2600 to 1200°K the diameter of the 100 plane increases from 260 Å to 500 Å; the major axis of the 211 plane increases from 400 Å to 750 Å; the 110 plane changes only slightly in size. (4) At 1200°K small 310 and 111 planes develop and step-like structures develop in the 111 zone between the 110 and 211 planes. (5) The rate at which the surface changes from one steady state configuration to another decreases with temperature. Below 1050°K this rate becomes too slow for convenient observation. (6) At 1050°K in one hour the 211 planes enlarge and the *W* atoms migrate in the 111 direction on this plane; the excess *W* is deposited on the adjoining paraboloidal surface.

EFFECT OF HIGH FIELDS AND TEMPERATURE IN DETERMINING  
SURFACE CONFIGURATION

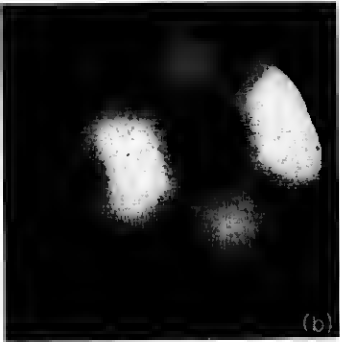
Figure 5 shows a series of photographs in which normally clean *W* was kept at 1400°K while approximately 8000 volts was applied to the anode for one minute to 39 minutes. The last photograph was taken after the *W* was heated to 1430°K for three minutes without an applied voltage. All photographs were taken with the *W* at room *T*. The voltage was adjusted until the total field emission was 30 microamps. As the treatment progresses: the 211 and 100 planes enlarge, while the 110 planes change their shape; the emission density from the 100 and surrounding regions decreases while that near the 111 and regions surrounding the 110-211 planes increases;



$T = 2600^{\circ}\text{K}$   $V = 0$   
 $\frac{10 \text{ SECONDS}}{V = 9230}$   $\frac{1}{5} \text{ SECOND}$   $I = 17 \mu\text{A}$



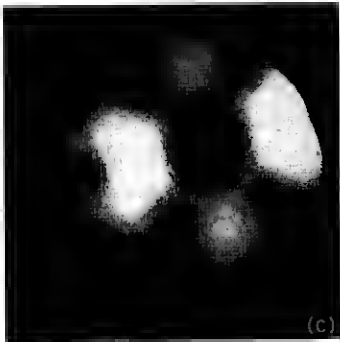
$T = 1600^{\circ}\text{K}$   $V = 0$   
 $\frac{20 \text{ MINUTES}}{V = 9220}$   $\frac{1}{5} \text{ SECOND}$   $I = 18 \mu\text{A}$



$T = 2400^{\circ}\text{K}$   $V = 0$   
 $\frac{3 \text{ MINUTES}}{V = 9230}$   $\frac{1}{5} \text{ SECOND}$   $I = 17 \mu\text{A}$



$T = 1200^{\circ}\text{K}$   $V = 0$   
 $\frac{20 \text{ MINUTES}}{V = 9170}$   $\frac{1}{5} \text{ SECOND}$   $I = 23.2 \mu\text{A}$

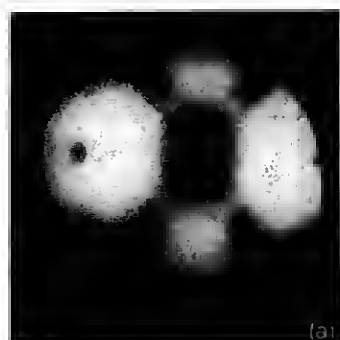


$T = 2000^{\circ}\text{K}$   $V = 0$   
 $\frac{20 \text{ MINUTES}}{V = 9220}$   $\frac{1}{5} \text{ SECOND}$   $I = 18 \mu\text{A}$



$T = 2400^{\circ}\text{K}$   $V = 0$   
 $\frac{3 \text{ MINUTES}}{V = 9230}$   $\frac{1}{5} \text{ SECOND}$   $I = 16.8 \mu\text{A}$

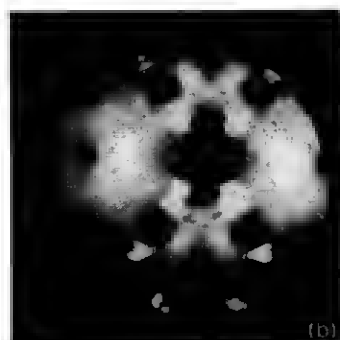
Fig. 4—Effect of temperature on size and shape of principal planes for clean *W*.



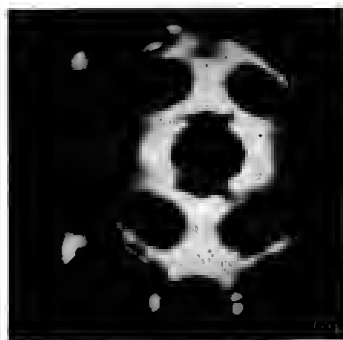
$T = 2400^{\circ}\text{K}$   $V = 0$   
 1 MINUTE  
 $V = 8900$   $I = 30 \mu\text{A}$   
 $2/5$  SECOND



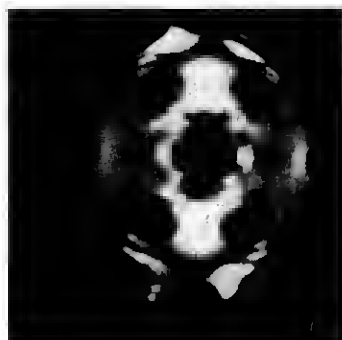
$T = 1400^{\circ}\text{K}$   $I = 50 \mu\text{A}$   $V = 8000$   
 21 MINUTES  
 $V = 7850$   $I = 30 \mu\text{A}$   
 $2/5$  SECOND



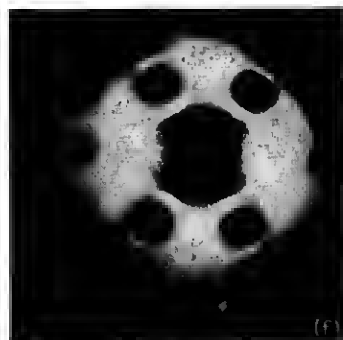
$T = 1400^{\circ}\text{K}$   $I = 17 \mu\text{A}$   $V = 8300$   
 1 MINUTE  
 $V = 8800$   $I = 30 \mu\text{A}$   
 $2/5$  SECOND



$T = 1400^{\circ}\text{K}$   $I = 25 \mu\text{A}$   $V = 7900$   
 39 MINUTES  
 $V = 8050$   $I = 30 \mu\text{A}$   
 $2/5$  SECOND



$T = 1400^{\circ}\text{K}$   $I = 30 \mu\text{A}$   $V = 8200$   
 6 MINUTES  
 $V = 8400$   $I = 30 \mu\text{A}$   
 $2/5$  SECOND



$T = 1430^{\circ}\text{K}$   $V = 0$   
 3 MINUTES  
 $V = 8500$   $I = 30 \mu\text{A}$   
 $2/5$  SECOND

Fig. 5—Effect of high fields at  $1400^{\circ}\text{K}$  on size and shape of principal planes for clean W.

in the early stages the intensity increases in the 111 zone "steps" and in the region beyond the 211 plane going toward the 111 plane.

We have repeated similar experiments, about 20 times, varying the temperature and field. The rate at which the changes take place increases with temperature and with field. The rate increases more rapidly than the first power, perhaps as the square or cube of the field. In one experiment the direction of the field was reversed; this did not affect the kind of changes nor the rates. In another experiment, the temperature was reduced to 800°K while a field of about 40 million volts/cm was applied; in one hour the 211 planes enlarged perceptibly, the intensity increased just beyond this plane in the 111 direction, and the "steps" in the 111 zone appeared. For fields  $> 40 \times 10^6$  volts/cm and  $T = 1500$  to  $1600^\circ\text{K}$ , most of the surface can be developed into planes; the highest emission comes from broad lines where the planes intersect; and the voltage necessary to obtain a given current is greatly reduced.

Many of these observations can be explained readily if we postulate that  $W$  atoms can be polarized and that such atoms will tend to move from low to high fields. The effects of such polarization forces will of course be superimposed on the forces which tend to hold the  $W$  atoms in certain crystalline positions. Consider normal clean tungsten after glowing at  $2400^\circ\text{K}$ , and concentrate attention on the 211 plane. In the previous section we concluded that above  $1050^\circ\text{K}$ ,  $W$  atoms are mobile on the surface and travel in the 111 direction until they reach the adjoining paraboloidal surface. A model of the 211 plane for  $W$  shows that, in the 111 direction, the atoms touch each other but the rows of atoms are separated by 1.635 atom diameters; hence we would expect that atoms on this plane could move quite readily in the 111 direction. Now consider the effects of a high field. At the edge of the 211 plane the field will be larger than average, while at the center it will be less than average so that the field must increase toward the edge. Hence there should be a net force due to the field tending to take atoms off the edge of the plane, and the rate at which the planes develop should be greater with a field than without. Furthermore the extent to which the plane develops should be greater with a field. Since the polarization and the field gradient are probably proportional to the field, and the force is the product of the two, one would expect the field effect to increase with the square of the field. Because the force on the polarized atom due to the field is away from the surface for both positive and negative fields, the field effects should be independent of the direction of the field.

The polarization postulate also explains the observation that after 39 minutes of applied field most of the emission comes from the 111 region and regions surrounding the 211 and 110 planes; and that the emission from

the regions surrounding the 100 plane, such as the 611 or 310 regions, is greatly reduced. Since the mobility of  $W$  atoms on 211 and 110 planes is greater than that on 100 planes, we conclude that the forces required to move a  $W$  atom on a 211 or 110 plane from a position of equilibrium to a neighboring position of equilibrium are less than those required to move an atom on a 100 plane. A study of models of these planes leads to the same conclusion. The field effect reduces the displacement work on all these planes, and hence we would expect that the 211 and 110 planes would change their shape faster than the 100 plane. The  $W$  atoms involved in such changes pile up in regions near their respective planes and thus increase the local field in such regions. Since the rate of migration increases rapidly with the field, these regions will grow at a still faster rate than before. Hence we would expect that such regions would pile up  $W$  atoms at the expense of other regions in which the migration rate started out more slowly. The experimental results, interpreted in this way, lead to the conclusion that high fields can result in movement of  $W$  atoms over distances of several thousand Angstroms.

We have made about five observations in which this effect continued even at room temperature. If by temperature and field treatment one obtains a pattern in which the emission from a few small spots materially exceeds that of other regions, and if the temperature is then reduced to 300°K while the voltage is kept on for hours, it is found that one or two of these spots will grow in size and intensity while other spots and regions get relatively less intense.

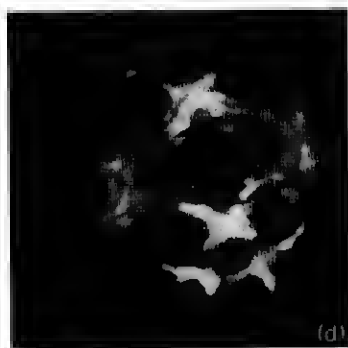
In such cases and in all cases of enhanced local field emission, the pattern can be brought back toward the normal condition by merely glowing the point at temperatures near 1000°K. The more the pattern differed from the normal one, the lower the temperature required to observe changes back toward the normal. One instance of the tendency to approach a normal pattern is that of the last photo in Fig. 5. A series of photos showing this tendency is given in Fig. 6.

#### EFFECT OF TEMPERATURE IN CHANGING AN ABNORMAL TO A NORMAL PATTERN

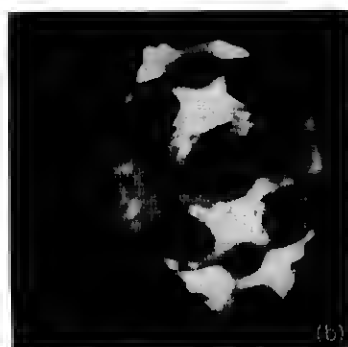
Figure 6 shows first a pattern of normal clean  $W$  for 2400°K; then follows a pattern produced by treatment at 1200°K with 8900 volts applied for 90 min. During this time the emission increased from 15 to 31 microamps; the next four patterns show the effect of glowing at successively higher temperatures for about an hour. A comparison of photos h and c shows that at 900°K the changes are slight: only a few of the brighter spots near the perimeter of the 110 and 211 planes have decreased in intensity.



$T = 2400^{\circ}\text{K}$        $V = 0$   
 3 MINUTES  
 $V = 9250$        $I = 14.5 \mu\text{A}$   
 $\frac{1}{5}$  SECOND



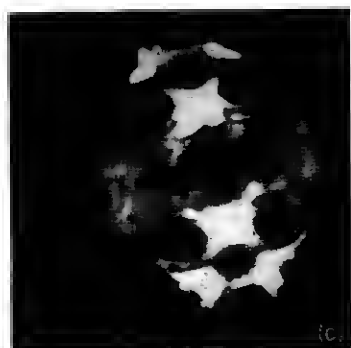
$T = 1000^{\circ}\text{K}$        $V = 0$   
 90 MINUTES  
 $V = 8940$        $I = 21 \mu\text{A}$   
 $\frac{1}{5}$  SECOND



$T = 1200^{\circ}\text{K}$        $I = 15 \text{ TO } 31 \mu\text{A}$        $V = 8900$   
 90 MINUTES  
 $V = 8840$        $I = 31 \mu\text{A}$   
 $\frac{1}{5}$  SECOND



$T = 1100^{\circ}\text{K}$        $V = 0$   
 60 MINUTES  
 $V = 8970$        $I = 17.5 \mu\text{A}$   
 $\frac{1}{5}$  SECOND



$T = 900^{\circ}\text{K}$        $V = 0$   
 60 MINUTES  
 $V = 8870$        $I = 28 \mu\text{A}$   
 $\frac{1}{5}$  SECOND



$T = 1210^{\circ}\text{K}$        $V = 0$   
 60 MINUTES  
 $V = 9000$        $I = 15 \mu\text{A}$   
 $\frac{1}{5}$  SECOND

Fig. 6—Effect of temperature in changing an abnormal to a normal pattern.



That the surface has changed detectably is shown by the fact that at room  $T$  the emission decreased from 31 to 28  $\mu a$  even though  $V$  increased from 8840 to 8870 volts. This means that the abnormal "bumps" have decreased slightly. These effects get progressively more pronounced as the glowing  $T$  was increased to 1200°K. The 611 region is now the brightest; the small 310 and 111 planes are still poor emitters. A continuation of the test showed that the 111 plane became normal after one hour at 1300°K. The 310 plane became normal after one hour at 1500°K. After one hour at 1600°K, the pattern looked like normal clean  $W$  except that the 100 and 211 planes were larger than in photo a of Fig. 6; it was similar to Fig. 4, photo d, after glowing at 1600°K.

## PART II: EMISSION AND ADSORPTION PROPERTIES OF Ba ON $W$

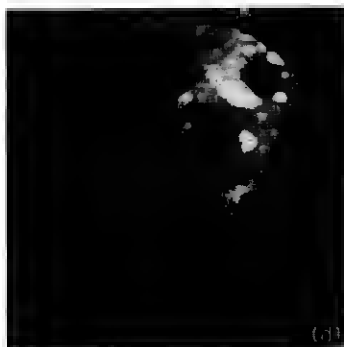
### FIELD EMISSION FROM Ba ON $W$

Figure 7 shows a series of photographs in which successive units or "shots" of Ba were vaporized onto the  $W$  point. The geometry of the tube was such that the greatest rate of deposition occurred on the upper right 611 region (Fig. 3b) and tapered off to zero on an "arc" which passes slightly to the left of the upper left 211, central 110, and lower right 211 planes. (Photo f of Fig. 7) In this series a "shot" of Ba was produced by heating the Ba coil with 2.4 amps for one minute. Later calculations will show that one "shot" deposited about 0.5 to 0.7 of a monolayer in the 611 region so that 7 shots deposited 3 to 5 layers in this region and deposited about 1 layer near the "arc" region.

The first photo shows clean tungsten treated so as to enlarge the 100 and 211 planes and to modify the shape of the 110 plane; the remainder of the surface is approximately on a paraboloid. In these latter regions the emission density is nearly uniform. In the 110 plane on the negative, there is a clear but faint ellipse. This ellipse is enhanced by the Ba in photos b, c, and d. We believe this ellipse to be due to the edge of a 110 plane which extends over only part of the larger underlying 110 plane. At this edge the local field is larger than in nearby regions and hence produces slightly greater emissions even on clean  $W$ . When Ba is deposited on this plane the edge serves as a nucleation center for Ba clusters even at 300°K. Prominent clusters also appear on the edges of the 211 planes in photos b, c, and d. Clusters also appear on the paraboloidal surfaces. The existence of these clusters shows that Ba atoms can move over a short distance—about 200 Å—even at room temperature.



$T = 1430^{\circ} \text{K}$        $V = 0$   
 $\frac{3 \text{ MINUTES}}{V = 6500}$        $\frac{I = 30 \mu\text{A}}{2/5 \text{ SECOND}}$



Ba COIL      2.4 AMPERES  
 $\frac{3 \text{ MINUTES}}{V = 3150}$        $\frac{I = 50 \mu\text{A}}{2/5 \text{ SECOND}}$



Ba COIL      2.4 AMPERES  
 $\frac{1 \text{ MINUTE}}{V = 5000}$        $\frac{I = 70 \mu\text{A}}{2/5 \text{ SECOND}}$



Ba COIL      2.4 AMPERES  
 $\frac{5 \text{ MINUTES}}{V = 3000}$        $\frac{I = 50 \mu\text{A}}{2/5 \text{ SECOND}}$



Ba COIL      2.4 AMPERES  
 $\frac{2 \text{ MINUTES}}{V = 3370}$        $\frac{I = 50 \mu\text{A}}{2/5 \text{ SECOND}}$



Ba COIL      2.4 AMPERES  
 $\frac{7 \text{ MINUTES}}{V = 3100}$        $\frac{I = 50 \mu\text{A}}{2/5 \text{ SECOND}}$

Fig. 7—Patterns for successively increasing amounts of Ba on W with enlarged planes.

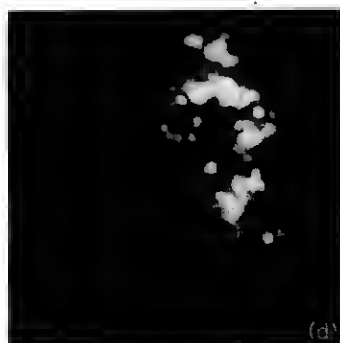
## FORMATION AND DISAPPEARANCE OF CRYSTALLITES

As the number of Ba shots increases in Fig. 7, a large dark region develops and enlarges from the right 100 region. This is due to the well known fact that when the Ba concentration exceeds one monolayer the work function increases. If the Ba atoms remained where they were deposited, one would expect the patterns to consist of broad bright arcs whose centers were at the region of greatest deposition and whose radii would increase with amount deposited; for 7 shots of Ba one would expect a narrow bright arc of nearly maximum possible radius. Such an arc does indeed appear after 6 and 7 shots; but the regions with more than a monolayer are not dark as expected; instead there appear in these regions intensely bright large area emission centers. These just begin to show after 3 shots and become more prominent for 4 to 7 shots. These bright emission centers have properties different from those of the clusters previously described; they are larger, may appear on any plane, are in a continuous state of flicker even at 300°K, disappear at much lower glowing temperatures and can be observed at much lower applied voltages. In accord with Haefer,<sup>7</sup> we believe that they are due to Ba crystals which grow normal to the surface; hence the term crystallites seems appropriate. At the crystallites the local field should be much greater than the average field and hence they should be observable at low applied voltages. Different crystallites should have a range of sizes and hence a range of spot sizes. Crystallites should occur only for Ba concentrations greater than monolayers and hence should be nearly independent of the underlying tungsten. Because of the very high current densities through a crystallite, one would expect a considerable increase in local temperature, perhaps even to the melting point of Ba which would change the size and shape of the crystallite and hence the emission; this accounts for the flickering and agrees with the observation that the amount of flickering increases with the applied voltage and emission current. If the crystallites are solid Ba they should evaporate more easily than Ba clusters adsorbed on W. Furthermore the existence of similar crystallites for evaporated films has been deduced from electron diffraction experiments. Hence the evidence for crystallites is quite good.

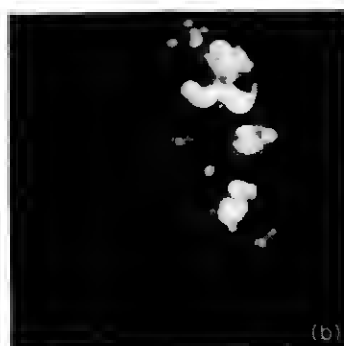
Figure 8 shows the evidence for the disappearance of crystallites in the temperature range 370 to 615°K. Note that, as  $T$  increases from 370 to 510°K, the voltage required to get 50 microamps decreases from 3150 to 2500. Note also that up to 615°K no detectable amount of Ba migrates into the region beyond the outermost arc. The intensity of this arc decreases, presumably because  $V$  is decreased.



$T = 370^{\circ}\text{K}$        $V = 2500$   
 $\frac{4 \text{ MINUTES}}{V = 2950}$        $L = 50 \mu\text{A}$   
 $\frac{2}{5} \text{ SECOND}$



$T = 450^{\circ}\text{K}$        $V = 0$   
 $\frac{5 \text{ MINUTES}}{V = 2650}$        $L = 50 \mu\text{A}$   
 $\frac{2}{5} \text{ SECOND}$



$T = 400^{\circ}\text{K}$        $V = 2500$   
 $\frac{5 \text{ MINUTES}}{V = 2900}$        $L = 50 \mu\text{A}$   
 $\frac{2}{5} \text{ SECOND}$



$T = 510^{\circ}\text{K}$        $V = 2300$   
 $\frac{6 \text{ MINUTES}}{V = 2500}$        $L = 50 \mu\text{A}$   
 $\frac{2}{5} \text{ SECOND}$



$T = 420^{\circ}\text{K}$        $V = 2400$   
 $\frac{10 \text{ MINUTES}}{V = 2900}$        $L = 70 \mu\text{A}$   
 $\frac{2}{5} \text{ SECOND}$



$T = 615^{\circ}\text{K}$        $V = 2300$   
 $\frac{5 \text{ MINUTES}}{V = 2570}$        $L = 50 \mu\text{A}$   
 $\frac{2}{5} \text{ SECOND}$

Fig. 8—The disappearance of crystallites from 370 to 615°K.

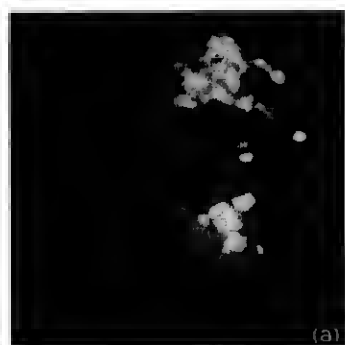
MIGRATION OF Ba ON *W*

Starting at about 800°K, Ba migrates over large distances—from one side of the paraboloid to the other or about 4000 Å. Figure 9 shows the steps in the migration process and the early stages of evaporation. The migration process can be followed continuously by observing the screen for moderate *V* between 800 and 1000°K. Migration is essentially complete after five minutes at 1045°K. By then the crystallites have disappeared completely and with them abnormally high local fields. It is therefore possible to compute the field from the applied voltage. Then, as explained above, values of  $\varphi$  and  $\theta$  averaged for the whole surface can be computed. In this way we find that for photos c and d in Fig. 9,  $\varphi = 2.00$  and  $\theta$  is about 1.00.

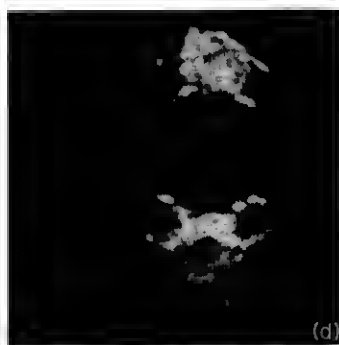
EVAPORATION OF Ba ON *W*

For  $T \geq 1200^\circ$  evaporation can be observed in five minutes. This is evidenced by the fact that after such glowing the value of *V* required for a given current increases. The details of the evaporation are continued in Fig. 10. From the values of *V* and *i*, values of  $\varphi$  and  $\theta$  have been calculated and are shown in TABLE I. From this table it appears that nearly all the Ba is evaporated in five minutes at 1600°K.

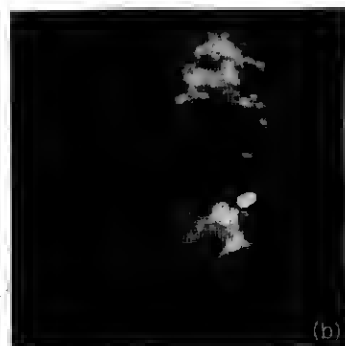
Further information on how the evaporation rate at a given *T* varies with  $\theta$  can be deduced from experiments for which no photos are shown. Suppose, in the above series of experiments, the point had been glowed for twenty minutes instead of five minutes, the calculated Ba concentration  $\theta$  would have reached a somewhat lower value than .80, say .75. Still further glowing would have reduced  $\theta$  only slightly. From this we conclude that at  $T = 1200$  and  $\theta = .75$  the rate of evaporation or  $d\theta/dt$  is so small that additional glowing for twenty minutes reduces  $\theta$  by small amounts. If now *T* is raised to 1300°K for one minute,  $\theta$  is substantially reduced, perhaps to .65. After five minutes at 1300°K,  $\theta$  might be .55. After twenty minutes at 1300,  $\theta$  might be .51. Long times at 1300°K might reduce  $\theta$  to .50. Only by raising *T* above 1300°K could  $\theta$  be substantially reduced below .50. These observations suggest that the rate of evaporation of Ba on *W* depends not only on *T* but also on  $\theta$ : for a constant *T* it is substantially 0 for all values of  $\theta$  less than a critical value  $\theta_c$ . Above  $\theta_c$ , the evaporation rate increases rapidly with  $\theta$ , perhaps exponentially. Hence the probability of evaporation of a particular Ba atom depends on the proximity of neighboring atoms. This must mean that the forces between adsorbed Ba atoms are comparable to though smaller than the forces between Ba and *W*. A plot of the  $\theta$  values in Table I vs *T* would show that  $\theta_c$  varies linearly with *T* between 1130 and 1430 or between  $\theta = 1.00$  and .18.



$T = 800^{\circ}\text{K}$        $V = 2400$   
 $\frac{6.5 \text{ MINUTES}}{V = 2800}$        $\frac{I = 50 \mu\text{A}}{2\frac{1}{5} \text{ SECOND}}$



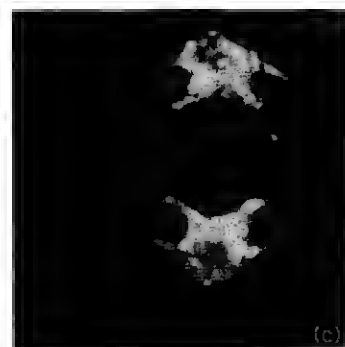
$T = 1130^{\circ}\text{K}$        $V = \text{VARIED}$   
 $\frac{5 \text{ MINUTES}}{V = 2850}$        $\frac{I = 50 \mu\text{A}}{2\frac{1}{5} \text{ SECOND}}$



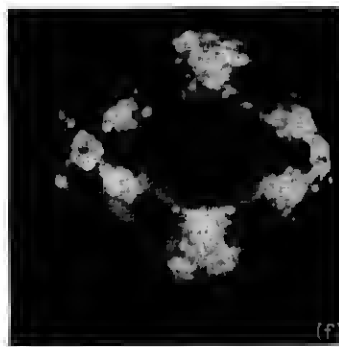
$T = 940^{\circ}\text{K}$        $V = 0$   
 $\frac{5 \text{ MINUTES}}{V = 2650}$        $\frac{I = 50 \mu\text{A}}{2\frac{1}{5} \text{ SECOND}}$



$T = 1210^{\circ}\text{K}$        $V = 0$   
 $\frac{5 \text{ MINUTES}}{V = 3250}$        $\frac{I = 50 \mu\text{A}}{2\frac{1}{5} \text{ SECOND}}$

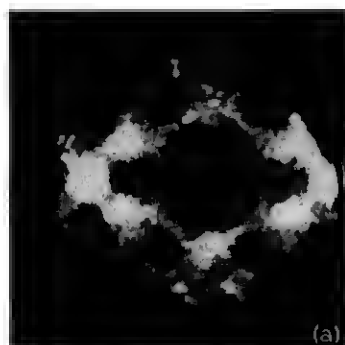


$T = 1045^{\circ}\text{K}$        $V = 0$   
 $\frac{5 \text{ MINUTES}}{V = 2800}$        $\frac{I = 50 \mu\text{A}}{2\frac{1}{5} \text{ SECOND}}$

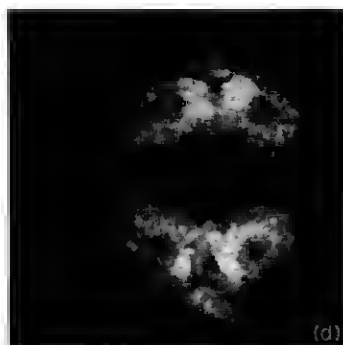


$T = 1275^{\circ}\text{K}$        $V = 0$   
 $\frac{8 \text{ MINUTES}}{V = 4400}$        $\frac{I = 50 \mu\text{A}}{2\frac{1}{5} \text{ SECOND}}$

Fig. 9—Migration of Ba on W from 800 to 1045°K. Evaporation of Ba on W from 1130 to 1275°K.



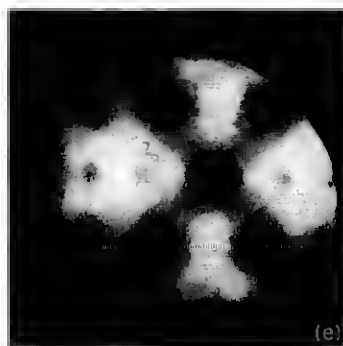
$T = 1330^{\circ}\text{K}$   $V = 0$   
 5 MINUTES  
 $V = 5000$   $I = 50 \mu\text{A}$   
 $2/5$  SECOND



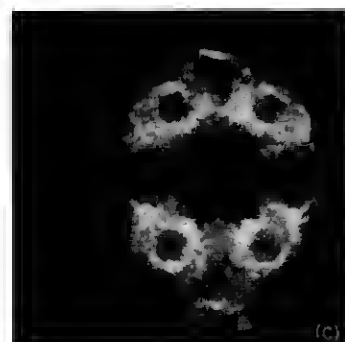
$T = 1515^{\circ}\text{K}$   $V = 0$   
 5 MINUTES  
 $V = 8350$   $I = 70 \mu\text{A}$   
 $1/5$  SECOND



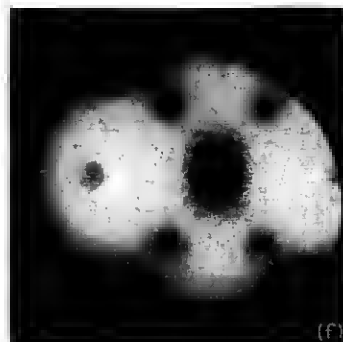
$T = 1360^{\circ}\text{K}$   $V = 0$   
 5 MINUTES  
 $V = 6000$   $I = 50 \mu\text{A}$   
 $2/5$  SECOND



$T = 1670^{\circ}\text{K}$   $V = 0$   
 3 MINUTES  
 $V = 9250$   $I = 27 \mu\text{A}$   
 $2/5$  SECOND



$T = 1430^{\circ}\text{K}$   $V = 0$   
 5 MINUTES  
 $V = 7130$   $I = 70 \mu\text{A}$   
 $1/5$  SECOND



$T = 2200^{\circ}\text{K}$   $V = 0$   
 1 MINUTE  
 $V = 9000$   $I = 30 \mu\text{A}$   
 $2/5$  SECOND

Fig. 10—Evaporation of Ba on W from 1330 to 1670°K.

## TEMPERATURE EFFECT ON CLUSTERS

The photos in Figs. 9 and 10 show that, for all values of  $\theta$  from 1.0 to .10, the emission comes largely from clusters. It is interesting to observe, but difficult to portray in photographs, what happens if the temperature is raised above room  $T$  but kept below that at which it had previously been heated to reduce  $\theta$ . As a specific instance we choose a case in which the treatment  $T$  was 1380°K for five minutes—photo b in Fig. 10—for which  $\theta = .28$ . With an applied voltage at  $T = 300^\circ\text{K}$ , the whole pattern and the clusters in particular are very steady. If  $T$  is now raised to about 700°K, the clusters bordering on the 211 planes and those in the 111 zone appear to be agitated: the brightness of any one cluster fluctuates up and down and the center of the cluster moves over about half a cluster diameter. Clusters in other regions are perfectly steady. As  $T$  is raised the 211 clusters agitate more violently and the clusters in nearby regions begin to agitate. At still higher  $T$ , the clusters in the 111 region begin to agitate but those surround-

TABLE I  
DEPENDENCE OF  $\varphi$  (AVERAGE WORK FUNCTION) AND  $\theta$  (LAYERS OF Ba) ON  
TEMPERATURE AND TIME

$T$ in °K.....	1045	1130	1210	1275	1330	1380	1430	1515	1670	2200
$t$ in min.....	5	5	5	6	5	5	5	5	3	1
$\varphi$ volts.....	1.98	2.00	2.20	2.47	2.81	3.30	3.70	4.10	4.53	4.40
$\theta$ .....	$\sim 1.0$	$\sim 1.0$	.80	.62	.46	.28	.18	.08	$\sim .00$	.00

ing the 100 plane are still steady. For  $T$  near 800°K all clusters show some agitation. At 1045°K, the clusters near the 110, 211, and 111 planes agitate so violently that individual clusters can no longer be distinguished but merge into one another producing bright bands which presumably reveal contours on the tungsten surface. However, the clusters in the regions surrounding the 100 plane agitate so slowly that in a photo of  $\frac{1}{8}$  sec exposure they appear to be stationary. Photo a, Fig. 11 shows the result. Photo b shows the pattern immediately afterward at  $T = 300^\circ\text{K}$ . These observations can be repeated as often as one pleases.

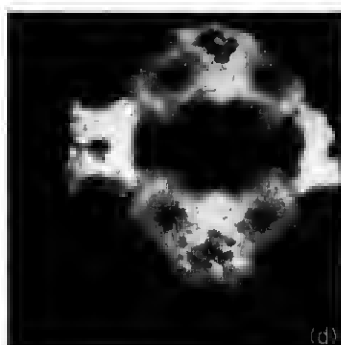
EFFECT OF FIELD ON THE REDISTRIBUTION OF Ba ON  $W$ 

Photos c to f of Fig. 11 show that fields of 30 to 40 million volts/cm can redistribute some Ba from the 110, 211 and 111 regions to the regions surrounding 100. Photo c shows the pattern after glowing at 1430°K for five minutes with  $V = 0$ . Photo d shows the pattern at  $T = 800^\circ\text{K}$  after 3 min. with  $T = 800^\circ\text{K}$  and  $V = 7380$  volts. When  $T$  was reduced to 300°K, the pattern did not change appreciably. However, when  $T$  was kept at 800°K for three minutes with  $V = 0$ , the pattern changed drastically as shown in photo e. Photo f shows that the redistribution is not the result of glowing

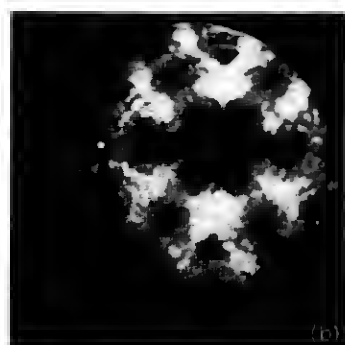




$T = 1380^{\circ}\text{K}$      $V = 0$     5 MINUTES  
 $T = 1045^{\circ}\text{K}$      $V = 6900$     5 MINUTES  
 $T = 1045^{\circ}\text{K}$      $I = 70 \mu\text{A}$      $V = 7100$   
     $\frac{1}{5}$  SECOND



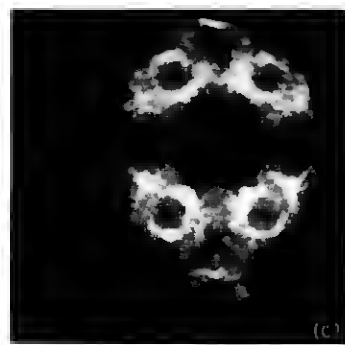
$T = 800^{\circ}\text{K}$      $V = 7360$   
    3 MINUTES  
 $T = 800^{\circ}\text{K}$      $I = 70 \mu\text{A}$      $V = 8000$   
     $\frac{1}{5}$  SECOND



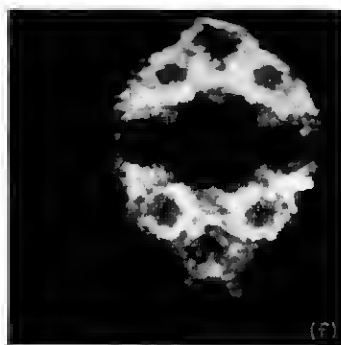
   NO TREATMENT  
 $T = 300^{\circ}\text{K}$      $I = 70 \mu\text{A}$      $V = 7750$   
     $\frac{1}{5}$  SECOND



$T = 800^{\circ}\text{K}$      $V = 0$   
    3 MINUTES  
 $T = 300^{\circ}\text{K}$      $I = 70 \mu\text{A}$      $V = 7370$   
     $\frac{1}{5}$  SECOND



$T = 1430^{\circ}\text{K}$      $V = 0$   
    5 MINUTES  
 $T = 300^{\circ}\text{K}$      $I = 70 \mu\text{A}$      $V = 7130$   
     $\frac{1}{5}$  SECOND



$T = 1430^{\circ}\text{K}$      $V = 0$     1 MINUTE  
 $T = 800^{\circ}\text{K}$      $V = 0$     3 MINUTES  
 $T = 300^{\circ}\text{K}$      $I = 70 \mu\text{A}$      $V = 7320$   
     $\frac{1}{5}$  SECOND

Fig. 11—Effect of temperature and field on the agitation of clusters and the redistribution of Ba. At 800 to 1000°K, Ba clusters are violently agitated near 211 and 111 planes but relatively stationary near 100 planes. High fields cause Ba to migrate from 111 and 211 regions to 100 regions.

at 800°K. To get the redistribution effect it is necessary to have both a high  $T$  and a high  $V$ .

It is fascinating and instructive to watch this redistribution progress slowly. To do this we start with a pattern like that in photo e with  $T = 300^\circ\text{K}$  and  $V = 7370$  volts. The clusters are steady everywhere.  $T$  is then raised to 800°K and the pattern observed for three to ten minutes. At first the clusters in the 110, 211, and 111 regions are in violent agitation while

TABLE II  
SUMMARY OF ADSORPTION PROPERTIES FOR FIVE PLANES ON A SINGLE CRYSTAL

Plane.....	110	211	100	111	611
Clean W					
Approximate $\phi$ in volts.....	>4.9	4.8	4.6	4.40	4.2
Size in Å for $T = 2400^\circ\text{K}$ .....	$1700 \times 1300$	400	260	<20	<20
Size in Å for $T = 1200^\circ\text{K}$ .....	$1700 \times 1100$	750	500	75	<20
Size for large $T$ and $F$ .....	Changes shape	1300	800	400	<20
$^\circ\text{K}$ for $W$ migration, $V = 0$ .....	1050	1050	1200		
$^\circ\text{K}$ for $W$ migration $V = 9000$ ....	800	800			
Ba on W; $\theta < 1$					
Size of clusters in Å.....	50 to 200; median 100	100			
$^\circ\text{K}$ for cluster formation.....	300	370		300	300
$^\circ\text{K}$ for cluster disappearance.....	370	420			
$^\circ\text{K}$ for Ba migration.....	370	420	800	~500	~600
$^\circ\text{K}$ for evaporation: depends on $\theta$ ..	1050 to 1600				
Ba on W; $\theta > 1$					
Size of crystallites in Å.....	200 to 600; median 400	400			
$^\circ\text{K}$ for crystal formation.....	300	300		300	300
$^\circ\text{K}$ for crystal disappearance.....	600	600		800	800

the few clusters in the 100 region are stationary. In ten seconds a few more clusters appear in the 100 region. When a new cluster appears it seems to do so suddenly. One gets the impression that one cluster pushed a neighboring one closer to the 100 plane or that one cluster grew at the expense of material from a neighboring one. Gradually as the concentration of clusters in the 100 region increases, the brightness of this region increases while the brightness in the 110, 211, and 111 regions decreases. A steady state is reached in three to five minutes.

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